2806 *Organometallics* **1996,** *15,* 2806−2809

$[Rh(\mu\text{-}OH)(PiPr_3)_2]_2$: Versatile Tool for the Binding of Alkynyl, Diynyl, and Diyndiyl Ligands to an Electron-Rich Rhodium(I) Center[†]

Olaf Gevert, Justin Wolf, and Helmut Werner*

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Received February 14, 1996[⊗]

The reaction of $[RhCl(PiPr_3)_2]_2$ (**1**) with NaOH under phase-tranfer conditions afforded the labile and extremely air-sensitive hydroxorhodium(I) complex $[Rh(\mu\text{-}OH)(PiPr_3)_2]_2$ (**2**) in 80% yield. The X-ray crystal structure analysis of **2** confirmed the dimeric nature of the molecule containing a nearly planar Rh_2O_2 unit. Compound **2** reacted with CO to yield *trans*-$[Rh(OH)(CO)(PiPr_3)_2]$ (**4**) and with $PhC\equiv CSiMe_3$, in the presence of pyridine or CO, to give *trans*-$[Rh(C\equiv CPh)(py)(PiPr_3)_2]$ (**5**) and *trans*-$[Rh(C\equiv CPh)(CO)(PiPr_3)_2]$ (**6**), respectively. Treatment of **4** with $Me_3SiC\equiv CC\equiv CSiMe_3$ yielded the binuclear diyndiyl complex $[(PiPr_3)_2(CO)Rh(C\equiv CC\equiv C)Rh(CO)(PiPr_3)_2]$ (**7**), while the corresponding reaction of **4** with $Me_3SiC\equiv CC\equiv CSnPh_3$ gave the mononuclear product *trans*-$[Rh(C\equiv CC\equiv CSiMe_3)(CO)(PiPr_3)_2]$ (**8**). The X-ray crystal structure analysis of **7** revealed the presence of an almost linear $Rh-C_4-Rh$ linkage with the midpoint of the central C−C bond as a crystallographic center of symmetry.

Introduction

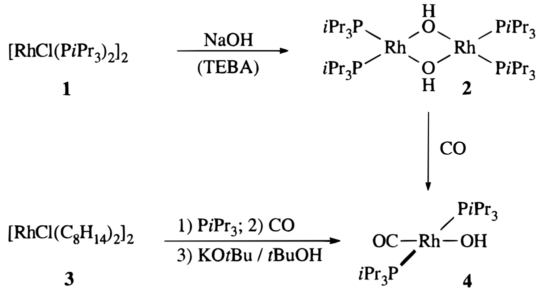
In the search for reactive halide-free bis(triisopropylphosphine)rhodium(I) complexes of general composition $[RhX(PiPr_3)_2]$, we recently described the preparation of $[Rh(\eta^2\text{-}O_2CCH_3)(PiPr_3)_2]$ and similar (carboxylato)rhodium(I) derivatives.[1] The four-coordinate acetato compound reacts with terminal alkynes $HC\equiv CR$ (R = Me, Ph) by oxidative addition to give the octahedral complexes $[RhH(C\equiv CR)(\eta^2\text{-}O_2CCH_3)(PiPr_3)_2]$, which either thermally or photochemically rearrange to the isomeric vinylidene species *trans*-$[Rh(\eta^1\text{-}O_2CCH_3)(=C=CHR)(PiPr_3)_2]$.[2] The synthesis of alkynyl(vinyl)- and alkynyl(butadienyl)rhodium(III) complexes from $[Rh(\eta^2\text{-}O_2CCH_3)(PiPr_3)_2]$ as starting material has also been reported.[3]

In continuation of this work we have now prepared the hydroxo derivative $[Rh(OH)(PiPr_3)_2]_2$ (**2**), which in the solid state is a dimer and which reacts at low temperatures with CO to yield the mononuclear compound *trans*-$[Rh(OH)(CO)(PiPr_3)_2]$ (**4**). Treatment of this highly reactive species with $SiMe_3$- and $SnPh_3$-substituted alkynes and diynes provides an entry into the chemistry of alkynyl-, diynyl- and diyndiylrhodium carbonyl complexes.

Results and Discussion

Reaction of the chloro compound **1**[4] in benzene with 20% aqueous NaOH in the presence of $[PhCH_2NEt_3]Cl$ (TEBA) results in a clean and nearly quantitative formation of the hydroxo complex **2** (Scheme 1). This process is somewhat similar to the synthesis of $[Rh(OH)(PPh_3)_2]_2$ from $[RhCl(PPh_3)_3]$ and KOH, recently reported by Alper et al.,[5] which also proceeds in benzene/water under biphasic conditions but does not need a phase-transfer catalyst. Compound **2** is an orange, very air-sensitive solid which is soluble in pentane and benzene, almost insoluble in acetone, and decomposes slowly in ether, THF, and chlorinated solvents. Also in the solid state and at room temperature, even under argon, slow decomposition occurs. The ^{31}P NMR spectrum of **2** in C_6D_6 displays a doublet at 61.3 ppm with a Rh−P coupling of 183.1 Hz which is almost identical to the $J(RhP)$ value of $[Rh(OH)(PPh_3)_2]_2$ (188 Hz).[5]

Scheme 1



The X-ray crystal structure analysis of **2** (Figure 1) confirms the dimeric nature of the molecule in which the two $Rh(PiPr_3)_2$ moieties are bridged by the hydroxy groups. This situation is similar to that found in both $[Rh(OH)(PPh_3)_2]_2$[6] and $[Rh(OH)(COD)]_2$ (COD = cycloocta-1,5-diene)[7] as well as in the chloro derivative **1**.[4b] The angles P1−Rh1−P2 and P3−Rh2−P4 in **2** are 105.68(5) and 105.57(5)°, respectively, and thus signifi-

---

[†] Dedicated to Professor Jörn Müller on the occasion of his 60th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

(1) (a) Schäfer, M.; Wolf, J.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1991**, 1341−1343. (b) Werner, H.; Schäfer, M.; Nürnberg, O.; Wolf, J. *Chem. Ber.* **1994**, *127*, 27−38.

(2) Schäfer, M.; Wolf, J.; Werner, H. *J. Organomet. Chem.* **1995**, *485*, 85−100.

(3) Werner, H.; Schäfer, M.; Wolf, J.; Peters, K.; von Schnering, H. G. *Angew. Chem.* **1995**, *107,* 213−215; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 191−194.

(4) (a) Preparation: Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985**, *287*, 395−407. (b) X-ray crystal structure: Binger, P.; Haas, J.; Glaser, G.; Goddard, R.; Krüger, C. *Chem. Ber.* **1994**, *127*, 1927−1929.

(5) Grushin, V. V.; Kuznetsov, V. F.; Bensimon, C.; Alper, H. *Organometallics* **1995**, *14*, 3927−3932.

(6) Brune, H.-A.; Hemmer, R.; Unsin, J.; Holl, K.; Thewalt, U. *Z. Naturforsch.* **1988**, *43b*, 487−490.

S0276-7333(96)00115-X CCC: $12.00

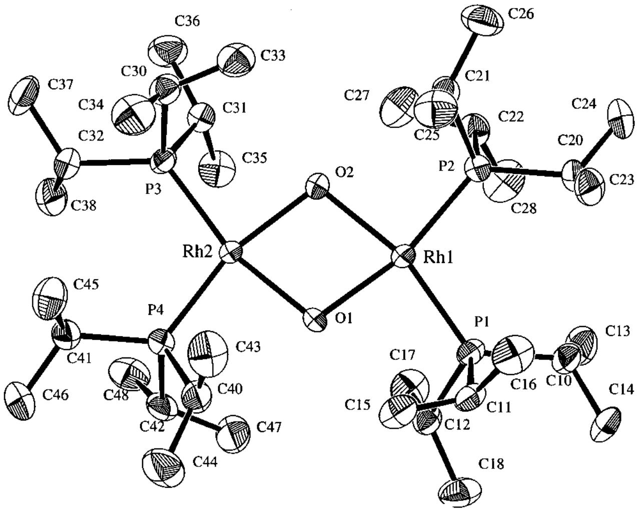


Figure 1.

Table 1. Selected Bond Distances and Angles with Esd's for Compound 2

	Bond Distances (Å)		
Rh1−P1	2.241(1)	Rh2−P3	2.238(1)
Rh1−P2	2.233(1)	Rh2−P4	2.229(1)
Rh1−O1	2.127(3)	Rh2−O1	2.106(4)
Rh1−O2	2.110(4)	Rh2−O2	2.122(4)
Rh1−Rh2	3.330(1)		
	Bond Angles (deg)		
P1−Rh1−P2	105.68(5)	P3−Rh2−P4	105.57(5)
P1−Rh1−O1	88.1(1)	P3−Rh2−O1	165.1(1)
P1−Rh1−O2	163.9(1)	P3−Rh2−O2	89.4(1)
P2−Rh1−O2	90.4(1)	P4−Rh2−O2	165.1(1)
P2−Rh1−O1	166.2(1)	P4−Rh2−O1	89.1(1)
O1−Rh1−O2	75.9(2)	O1−Rh2−O2	76.1(2)
Rh1−O1−Rh2	103.7(2)	Rh1−O2−Rh2	103.8(2)

cantly larger than in **1** [97.2(1)°].[4b] In contrast to **1** and $[Rh(OH)(PPh_3)_2]_2$, the central Rh_2O_2 core is not completely planar; the oxygen and rhodium atoms deviate by ±0.050(1) Å from the best plane calculated for this unit. The four phosphorus atoms are beneath this plane, the dihedral angle between the planes [P1, Rh1, P2] and [P3, Rh2, P4] being 9.6(1)°. The Rh−O bond lengths in **2** (mean value 2.116(4) Å; see Table 1) are somewhat larger than in the bis(triphenylphosphine) analogue [2.064(3) and 2.067(3) Å] and the same is true for the Rh−P distances.

The dimeric compound **2** reacts at low temperatures with CO by bridge cleavage to yield the mononuclear carbonyl complex **4** (Scheme 1) which has originally been prepared either from *trans*-$[RhCl(CO)(PiPr_3)_2]$ and NaO^iPr in 2-propanol[8] or from $[RhH(PiPr_3)_3]$ when used as a catalyst in the water-gas shift reaction.[9] We found that **4** is also accessible by a one-pot synthesis, starting with $[RhCl(C_8H_{14})_2]_2$ (**3**) via **1** and *trans*-$[RhCl(CO)(PiPr_3)_2]$[8,10] as intermediates. The final replacement of Cl^- by OH^- to give **4** proceeds with KO*t*Bu and *tert*-butyl alcohol without using a phase-transfer catalyst.

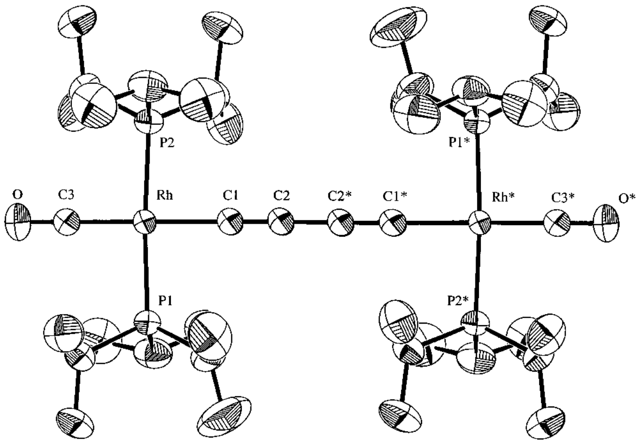
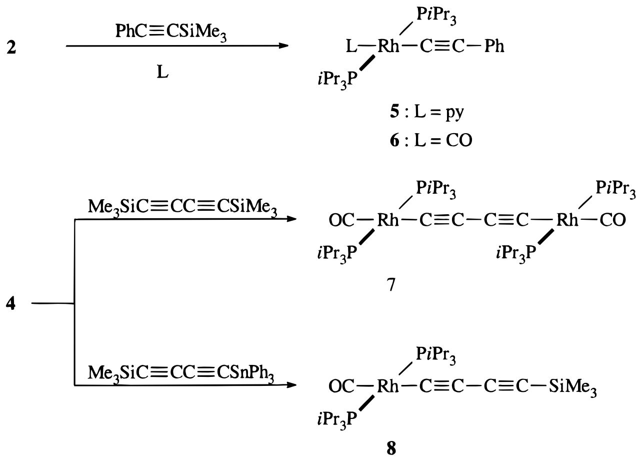


Figure 2.

Scheme 2



Most remarkably, both hydroxo compounds **2** and **4** are highly reactive toward silylated and stannylated alkynes and are thus excellent precursors for the synthesis of alkynyl-, diynyl- and diyndiylrhodium(I) derivatives (Scheme 2). Complex **2** reacts with $PhC{\equiv}CSiMe_3$ in the presence of Lewis bases such as pyridine or carbon monoxide to form the mononuclear compounds *trans*-$[Rh(C{\equiv}CPh)(py)(PiPr_3)_2]$ (**5**) and *trans*-$[Rh(C{\equiv}CPh)(CO)(PiPr_3)_2]$ (**6**), respectively. Other preparative routes to **5** and **6** have already been reported, using either $[RhH(C{\equiv}CPh)Cl(py)(PiPr_3)_2]$ or $[RhH(C{\equiv}CPh)(O_2CCH_3)(CO)(PiPr_3)_2]$ as starting materials.[2,11]

The hydroxo−carbonyl complex **4**, on treatment with a 0.5 molar equiv of $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$, affords the binuclear compound $[(PiPr_3)_2(CO)Rh(C{\equiv}CC{\equiv}C)Rh(CO)(PiPr_3)_2]$ (**7**) containing a "naked" C_4 bridge[12] in 75% yield. **7** is a yellow crystalline solid which is moderately air-stable and easily soluble in ether and hydrocarbon solvents. Since the IR and ^{13}C NMR spectra of **7** did not conclusively support the structural proposal for **7**, an X-ray crystal structural investigation was carried out. As shown in Figure 2, the two $Rh(CO)(PiPr_3)_2$ fragments are bridged by an almost perfectly linear C_4 unit. The midpoint of the C−C single bond of the C_4 bridge lies on a crystallographic center of symmetry, and therefore, only four halves of the molecule are found in the unit cell. As a consequence, both P_2RhCO planes

---

(7) (a) Preparation: Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126−127. (b) X-ray crystal structure: Selent, D.; Ramm, M. *J. Organomet. Chem.* **1995**, *485*, 135−140.

(8) Gregorio, G.; Pregaglia, G.; Ugo, R. *Inorg. Chim. Acta* **1969**, *3*, 89−93.

(9) Yoshida, T.; Okano, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 3411−3422.

(10) Busetto, C.; D'Alfonso, A.; Maspero, F.; Perego, G.; Zazzetta, A. *J. Chem. Soc., Dalton Trans.* **1977**, 1828−1834.

(11) Werner, H.; Wolf, J.; Garcia Alonso, F. J.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1987**, *336*, 397−411.

(12) For a short review on organometallics with "naked" C_n units, see: Lang, H. *Angew. Chem.* **1994**, *106*, 569−572; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547−550.

Table 2. Selected Bond Distances and Angles with Esd's for Compound 7

	Bond Distances (Å)		
Rh−C1	2.021(4)	Rh−P2	2.319(2)
Rh−C3	1.832(4)	C3−O1	1.143(5)
Rh−P1	2.323(2)	C1−C2	1.205(5)
		C2−C2*	1.388(7)
	Bond Angles (deg)		
P1−Rh−P2	175.70(3)	C1−Rh−C3	177.8(2)
P1−Rh−C1	88.6(1)	Rh−C1−C2	178.5(4)
P1−Rh−C3	91.7(1)	Rh−C3−O1	178.2(4)
P2−Rh−C1	87.6(1)	C1−C2−C2*	178.9(5)
P2−Rh−C3	92.2(1)		

[a] The midpoint of the bond C2−C2* is a center of symmetry, and therefore, the corresponding bond distances Rh−C1/Rh*−C1*, etc., and bond angles P1−Rh−P2/P1*−Rh*−P2*, etc., are identical.

lie parallel in the crystal and not perpendicular as one would expect due to the steric demand of the bulky phosphine groups. Not only the Rh−C1−C2 and C1−C2−C2* but also the Rh−C−O linkages are nearly linear while the P1−Rh−P2 axis is slightly bent (see Table 2). The bond lengths of the RhC_4Rh unit are comparable to those found in ReC_4Re[13] and RuC_4Ru complexes,[14] which have a piano-stool configuration. We note that besides **7** both cationic[15] and neutral[16] binuclear rhodium(III) complexes incorporating a RhC_4Rh linkage are known; however, they contain octahedrally coordinated Rh(III) centers.

From **4** and $Ph_3SnC{\equiv}CC{\equiv}CSiMe_3$ as starting materials, the mononuclear diynylmetal complex $[Rh(C{\equiv}CC{\equiv}CSiMe_3)(CO)(P\mathit{i}Pr_3)_2]$ (**8**) has been prepared. The silyl−stannyl diyne derivative was obtained via the lithium compound $Me_3SiC{\equiv}CC{\equiv}CLi$,[17] which is accessible from $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ and 1 equiv of CH_3Li.[18] In contrast to the ^{13}C NMR spectrum of **7**, in which only two slightly overlapping multiplets for the carbon atoms of the C_4 bridge are observed, the ^{13}C NMR spectrum of **8** displays four well-separated signals at δ 121.25, 103.0, 93.2, and 77.2 for the carbons of the C_4 chain. The first two of these signals are split into doublets-of-triplets due to Rh−C and P−C coupling. It should be mentioned that *trans*-$[Rh(C{\equiv}CC{\equiv}CPh)(CO)(P\mathit{i}Pr_3)_2]$, an analogue of compound **8**, is known and has recently been synthesized by stepwise treatment of $[Rh(\eta^2\text{-}CH_2C_6H_5)(P\mathit{i}Pr_3)_2]$ with CO and $HC{\equiv}CC{\equiv}CPh$.[19]

In summary, we have established a new route for the preparation of square-planar alkynyl-, diynyl- and diyndiylrhodium(I) complexes using either the highly reactive binuclear hydroxo-bridged species **2** or the corresponding mononuclear carbonyl derivative **4** as starting materials. The propensity of hydroxorhodium compounds to react with acidic substrates by forming new rhodium−element bonds has already been illustrated by Alper et al.,[5] who prepared $[C_5H_5Rh(PPh_3)_2]$, $[Rh(\mu\text{-}O_2CPh)(PPh_3)_2]$, and in particular the heterobinuclear complexes $[(PPh_3)_2Rh(\mu\text{-}CO)_2M(CO)C_5H_5]$ (M = Cr, Mo, W) from $[Rh(\mu\text{-}OH)(PPh_3)_2]_2$.

Experimental Section

All reactions were carried out under an atmosphere of argon by use of Schlenk tube techniques. The starting materials $[RhCl(P\mathit{i}Pr_3)_2]_2$ (**1**),[4a] $[RhCl(C_8H_{14})_2]_2$ (**3**),[20] and $Me_3SiC{\equiv}CC{\equiv}CSnPh_3$[17] were prepared as described in the literature. $PhC{\equiv}CSiMe_3$ and $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ were commercial products from Aldrich and ABCR. NMR spectra were recorded at room temperature on Varian 360 EM, Jeol FX 90 Q, Bruker AC 200, and Bruker AMX 400 instruments, and IR spectra on a Perkin-Elmer 1420 infrared spectrophotometer. Melting points were determined by DTA.

Preparation of $[Rh(\mu\text{-}OH)(P\mathit{i}Pr_3)_2]_2$ (2). A solution of **1** (160 mg, 0.17 mmol) in 10 mL of benzene was treated with 5 mL of 20% aqueous NaOH (saturated with argon) and TEBA (10 mg). Upon stirring of the reaction mixture for 20 min at room temperature, a change of color from violet to orange occurred. The organic phase was separated, washed with 5 mL of degassed H_2O, and then brought to dryness in vacuo. After the residue was extracted with 20 mL of pentane and the solvent removed from the extract, an orange solid was obtained: yield 123 mg (80%); mp 107 °C dec; ^1H NMR (C_6D_6, 200 MHz) δ 2.00 (m, 6H, $PC\mathit{H}CH_3$), 1.40 [dd, $J(PH) = 11.6$, $J(HH) = 7.3$ Hz, 36H, $PCHC\mathit{H}_3$], −2.77 (s, br, 1H, OH); ^{31}P NMR (C_6D_6, 81.0 MHz) δ 61.3 [d, $J(RhP) = 183.1$ Hz].

Preparation of *trans*-$[Rh(OH)(CO)(P\mathit{i}Pr_3)_2]$ (4). Method a. A solution of **2** (138 mg, 0.16 mmol) in 5 mL of pentane was stirred at −78 °C under a CO atmosphere. After 2−3 min an almost white solid precipitated, which was separated from the mother liquor, washed three times with 3 mL of pentane each, and dried: yield 139 mg (95%).

Method b. A suspension of **3** (272 mg, 0.38 mmol) in 7 mL of acetone was treated with $P\mathit{i}Pr_3$ (435 μL, 365 mg, 2.28 mmol) and stirred for 10 min at room temperature. A violet precipitate (consisting of **1**) was formed, which was separated from the solution, washed three times with 3 mL of acetone (0 °C) each, and then dissolved in 8 mL of benzene. Upon passing CO through this solution for 10−15 sec, a change of color from violet to pale yellow occurred. The solution was treated with $KO^t\!Bu$ (0.1 g, 1.0 mmol) and 1 mL of *t*BuOH and stirred for 16 h at room temperature. Thereafter, 3 mL of degassed H_2O was added, the two phases were separated, and the organic phase was washed twice with 3 mL of H_2O each and then filtered. The filtrate was brought to dryness in vacuo, and the residue was repeatedly washed with pentane and dried: yield 258 mg (72%). Compound **4** was identified by comparison of the ^1H NMR spectrum with published data.[9] ^{31}P NMR (C_6D_6, 36.2 MHz): δ 50.35 [d, $J(RhP) = 136.3$ Hz].

Formation of *trans*-$[Rh(C{\equiv}CPh)(py)(P\mathit{i}Pr_3)_2]$ (5) from 2. To a solution of **2** (50 mg, 0.06 mmol) in 0.5 mL of C_6D_6, placed in an NMR tube, was added $PhC{\equiv}CSiMe_3$ (20 μL, 0.10 mmol) and excess of pyridine (ca. 20 μL). After 24 h at room temperature, the ^{31}P NMR spectrum (36.2 MHz) displayed a doublett at 41.1 ppm [$J(RhP) = 150.9$ Hz] which by comparison was shown to correspond to **5**;[11] the yield was nearly quantitative.

Formation of *trans*-$[Rh(C{\equiv}CPh)(CO)(P\mathit{i}Pr_3)_2]$ (6) from 2. A solution of **2** (50 mg, 0.06 mmol) in 0.5 mL of C_6D_6, placed in an NMR tube, was treated with $PhC{\equiv}CSiMe_3$ (20 μL, 0.10 mmol) at room temperature. After argon was replaced by CO, the tube was sealed and stored for 4 h at 40 °C. The ^{31}P NMR spectrum (36.2 MHz) then displayed a doublet at 53.7 ppm [$J(RhP) = 126.0$ Hz] which by comparison was shown to correspond to **6**[2] with a yield nearly quantitative.

---

(13) Zhou, Y.; Seyler, J. W.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 8509−8510.

(14) Bruce, M. I.; Hinterding, P.; Tiekink, E. R. T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1993**, *450*, 209−218.

(15) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188−190.

(16) Rappert, T.; Nürnberg, O; Werner, H. *Organometallics* **1993**, *12*, 1359−1364.

(17) Bréfort, J. L.; Corriu, R. J. P.; Gerbier, P.; Guérin, C.; Henner, B. J. L.; Jean, A.; Kuhlmann, T.; Garnier, F.; Yassar, A. *Organometallics* **1992**, *11*, 2500−2506.

(18) Holmes, A. B.; Jennings-White, C. L. D.; Schulthess, A. H.; Akinde, B.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1979**, 840−842.

(19) Werner, H.; Gevert, O.; Steinert, P.; Wolf, J. *Organometallics* **1995**, *14*, 1786−1791.

(20) van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1973**, *14*, 92−95.

Table 3. Crystallographic Data for 2 and 7

formula	$C_{36}H_{86}O_2P_4Rh_2$ (**2**)	$C_{42}H_{84}O_2P_4Rh_2$ (**7**)
fw	880.75	950.80
cryst size, mm^3	0.48 × 0.43 × 0.55	0.20 × 0.30 × 0.30
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
cell dimens determn	25 reflns, $10° < \theta < 16°$	25 reflns, $8° < \theta < 19°$
a, Å	13.218(3)	11.430(9)
b, Å	16.275(3)	17.181(3)
c, Å	21.712(3)	13.012(8)
β, deg	104.730(4)	103.87(3)
V, Å^3	4517(2)	2481(2)
Z	4	2 ($^4/_2$)
d_{calcd}, g cm^{-3}	1.295	1.273
diffractometer	Enraf Nonius CAD4	
radiation (λ, Å)	Mo Kα (0.709 30)	
filter factor (Zr filter)	16.4	15.4
temp, °C	−50(2)	+20(2)
μ, mm^{-1}	0.890	0.816
scan method	ω/θ	ω/θ
2θ(max), deg	42	50
tot. no. of reflns scanned	4564	4558
no. of unique reflns	4302 [R(int) = 0.0426]	4328 [R(int) = 0.0658]
no. of obsd reflns [$I > 2(I)$]	3676	3588
no. of reflns used for refinement	4294	4327
no. of params refined	403	238
final R indices [$I > 2(I)$]	$R1 = 0.0258^a$ $wR2 = 0.0686$	$R1 = 0.0348^a$ $wR2 = 0.0927$
R indices (all data)	$R1 = 0.0408$ $wR2 = 0.0836^b$	$R1 = 0.0512$ $wR2 = 0.1033^b$
reflns:param ratio	10.7	18.2
resid electron density, e Å^{-3}	0.386/−0.370	0.790/−0.752

[a] Conventional R-factor: $R1 = \sum|F_o - F_c|/\sum F_o$ [for $F_o > 4\sigma(F_o)$]. [b] Weighted R-factor: $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, with $w^{-1} = \sigma^2(F_o)^2 + 0.0326P^2 + 7.1252P$ (**2**) and $w^{-1} = \sigma^2(F_o)^2 + 0.0604P^2 + 1.042P$ (**7**), where $P = (F_o^2 + 2F_c^2)/3$.

Preparation of *trans,trans*-[(P*i*Pr$_3$)$_2$(CO)Rh(C≡CC≡C)Rh(CO)(P*i*Pr$_3$)$_2$] (7). A solution of **4** (150 mg, 0.32 mmol) in 3 mL of methanol was treated with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ (31 mg, 0.16 mmol) at room temperature and then heated for 1 min under reflux. After the solution was cooled to room temperature, the solvent was removed in vacuo, and the residue was dissolved in 2 mL of acetone. Upon storing of this solution for 15 h at −78 °C, yellow crystals precipitated, which were filtered out, washed with 2 mL of acetone (−20 °C), and dried: yield 115 mg (75%); mp 128 °C dec; IR (KBr) ν(CO) 1934 cm^{-1}, ν(C≡C) not exactly located; ^{1}H NMR (C_6D_6, 400 MHz) δ 2.50 (m, 6H, PC*H*CH$_3$), 1.36 [dvt, N = 14.0, J(HH) = 7.2 Hz, 36H, PCHC*H*$_3$]; ^{13}C NMR (C_6D_6, 100.6 MHz) δ 196.0 [dt, J(RhC) = 58.4, J(PC) = 12.6 Hz, Rh*C*O], 109.5, 108.1 (both m, Rh*C*≡C and RhC≡*C*), 26.3 [vt, N = 22.0 Hz, P*C*HCH$_3$], 20.6 (s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6, 162.0 MHz) δ 54.1 [d, J(RhP) = 128.0 Hz]. Anal. Calcd for $C_{42}H_{84}O_2P_4Rh_2$: C, 53.05; H, 8.90; Rh, 21.65. Found: C, 53.06; H 9.17; Rh, 20.61.

Preparation of *trans*-[Rh(C≡CC≡CSiMe$_3$)(CO)(P*i*Pr$_3$)$_2$] (8). A solution of **4** (120 mg, 0.26 mmol) in 5 mL of benzene was treated with $Me_3SiC{\equiv}CC{\equiv}CSnPh_3$ (123 mg, 0.26 mmol) at room temperature and then heated for 1−2 min to 80 °C. After being cooled to room temperature the solution was worked up as described for **7**: yellow microcrystalline solid; yield 86 mg (58%); mp 64 °C dec; IR (KBr) ν(C≡C) 2150, 2105, ν(CO) 1940 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 2.39 (m, 6H, PC*H*CH$_3$), 1.21 [dvt, N = 14.0, J(HH) = 7.2 Hz, 36H, PCHC*H*$_3$], 0.08 (s, 9H, SiMe$_3$); ^{13}C NMR (C_6D_6, 100.6 MHz) δ 195.9 [dt, J(RhC) = 72.4, J(PC) = 13.1 Hz, Rh*C*O], 121.25 [dt, J(RhC) = 43.3, J(PC) = 22.1 Hz, Rh*C*≡C], 103.0 [dt, J(RhC) = 13.1, J(PC) = 2.5 Hz, RhC≡*C*], 93.2, 77.2 (both s, br, RhC≡C*C*≡C and *C*SiMe$_3$), 26.3 [vt, N = 21.6 Hz, P*C*HCH$_3$], 20.35 (s, PCH*C*H$_3$), 0.5 (s, SiMe$_3$); ^{31}P NMR (C_6D_6, 162.0 MHz) δ 53.6 [d, J(RhP) = 125.2 Hz]. Anal. Calcd for $C_{26}H_{51}OP_2RhSi$: C, 54.54; H, 8.98; Rh, 17.97. Found: C, 54.70; H 8.68; Rh, 18.25.

X-ray Structural Analyses of 2 and 7. Single crystals were grown from hexane (**2**) and toluene (**7**). Crystal data collection parameters are summarized in Table 3. Intensity data were corrected for Lorentz and polarization effects; for **2** a linear decay (loss of gain −6.2%) was taken into consideration. The structures were solved by direct methods (SHELXS-86). The positions of the hydrogen atoms (with the exception of O−H) were calculated according to ideal geometry (distance of C−H set at 0.95 Å) and were refined by the riding method. Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-93). For other details see Table 3.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (Grant SFB 347) and the Fonds der Chemischen Industrie for financial support. We also gratefully acknowledge support by Mrs. A. Spenkuch and Mr. U. Schmidt (technical assistance), Mrs. R. Schedl and Mr. C. P. Kneis (elemental analysis and DTA), Mrs. M. L. Schäfer, Mr. B. Stempfle, and Mr. C. Grünwald (NMR measurements), and Degussa AG (chemicals).

Supporting Information Available: Tables of data collection parameters, bond lengths and angles, positional and thermal parameters, and least-squares planes for **2** and **7** (13 pages). Ordering information is given on any current masthead page.

OM9601155